

Supplementary Information:

# Ultrafast Capture of Electron Ejected by the Photoionization Leading to the Formation of Charge-Separated State at High Energy Level.

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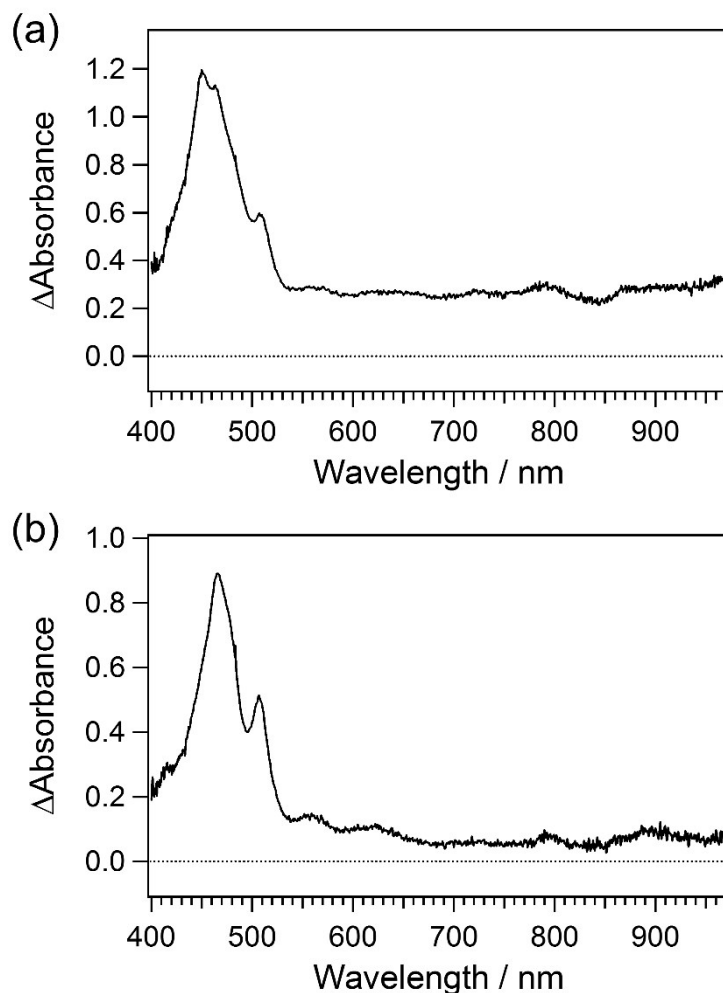
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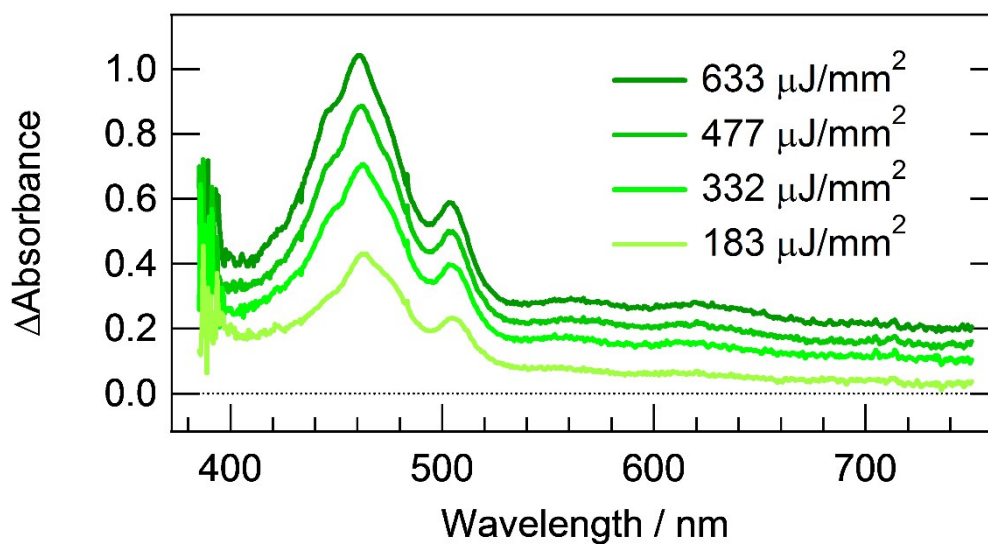
## S1. Evaluation of the solvated electron



**Figure S1.** Transient absorption spectra of pyrene in acetonitrile for (a) and cyclohexane for (b). The sample was excited with a picosecond laser pulse at 355 nm. The delay time was set to 100 ps.

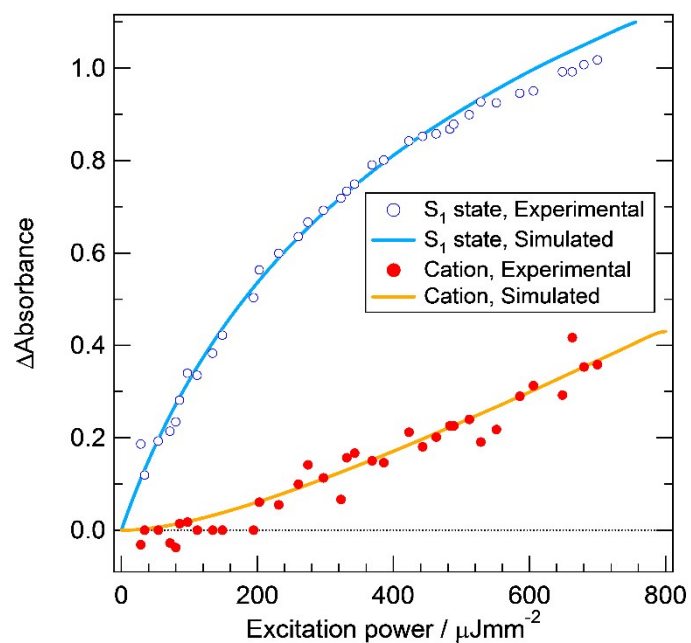
Figure S1 shows transient absorption spectra of pyrene in cyclohexane and acetonitrile excited with a picosecond laser pulse at 355 nm. In the panel a, the spectrum in acetonitrile shows very broad absorption in the entire visible and near-infrared region together with the strong absorption of the cation radical. This broad feature is not observed in the spectrum of pyrene in cyclohexane where the ionization does not take place. Thus, this broad absorption is ascribable to the solvated electron and the resultant dimer anion,  $(\text{ACN})_2^-$ .

## S2. Transient absorption spectra in methanol solution



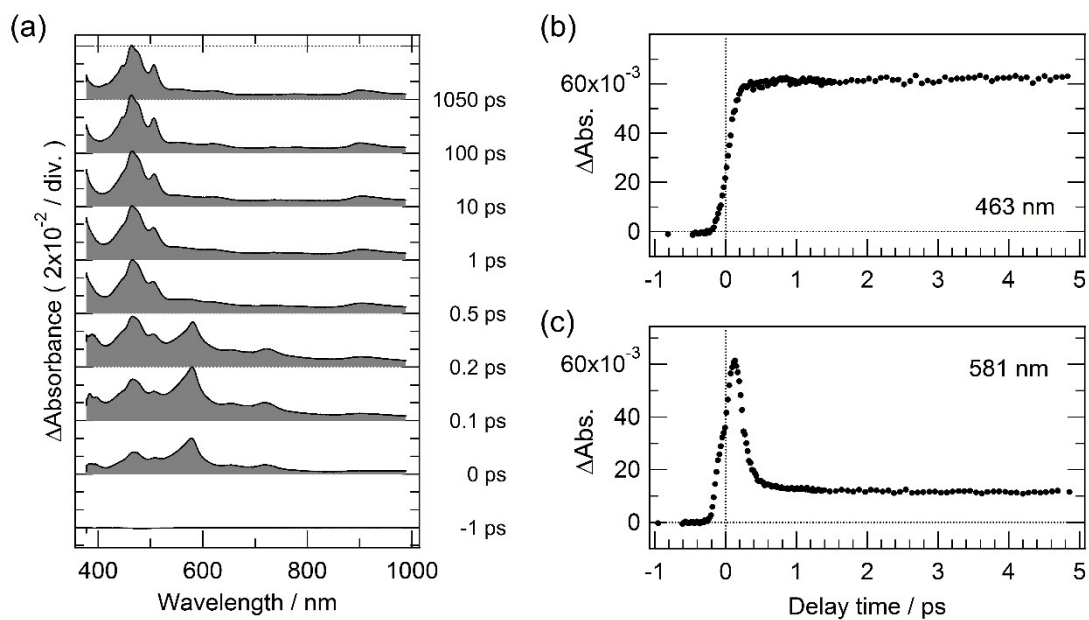
**Figure S2.** Transient absorption spectra of pyrene in methanol solution measured at different excitation intensities. The sample was excited with a picosecond laser pulse at 355 nm. The delay time was set to 100 ps.

### S3. Excitation power dependence in methanol solution



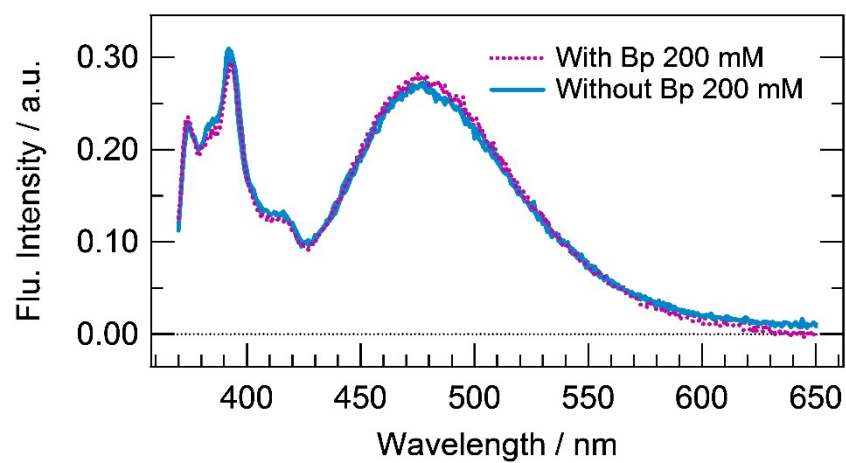
**Figure S3.** Excitation power dependence of absorbance of the S<sub>1</sub> state and that of the cation radical of pyrene in methanol solution. The detected transient absorbance was decomposed into the contributions of the S<sub>1</sub> state and cation radical on the basis of the numerical simulation. The ionization quantum yield in the higher state was estimated to be  $\sim 0.08$  in methanol from the numerical simulation.

#### S4. Transient absorption spectra under 340-nm excitation



**Figure S4.** (a) Transient absorption spectra of pyrene in acetonitrile solution excited with a femtosecond laser pulse at 340 nm. (b,c) Time profiles of transient absorbance monitored at 463 and 581 nm, which are respectively attributable to the absorption wavelengths of the  $S_1$  and  $S_2$  states. The excitation power was set to 1.10  $\mu\text{J}/\text{pulse}$ .

### S5. Evaluation of quenching effect of biphenyl on pyrene



**Figure S5.** Steady-state fluorescence spectra of pyrene in acetonitrile solution in the presence and absence of biphenyl (0.2 M).